Spectrochimica Acta Part B 125 (2016) 18–24

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

# Spectroscopic characterization of the plasmas formed during the deposition of ZnO and Al-doped ZnO films by plasma-assisted pulsed laser deposition

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ARTICLE INFO

*Article history:*
Received 21 June 2016
31 August 2016
Accepted 9 September 2016
Available online 10 September 2016

*Keywords:*
Plasma emission
Optical emission spectroscopy
Plasma species
Plasma-assisted deposition
Al-doped ZnO

ABSTRACT

An oxygen-zinc plasma and an oxygen-zinc-aluminum plasma are formed by pulsed laser ablation of a Zn target or pulsed laser co-ablation of a Zn target and an Al target in an electron cyclotron resonance (ECR) discharge-generated oxygen plasma for the deposition of ZnO and Al-doped ZnO (AZO) films. The plasmas are characterized spectroscopically by time-integrated and time-resolved optical emission spectroscopy. Both the oxygen-zinc plasma and the oxygen-zinc-aluminum plasma contain excited species originally present in the working $O_2$ gas and energetic species ablated from the targets. The optical emission of the oxygen-zinc-aluminum plasma is abundant in the emission bands of oxygen molecular ions and the emission lines of mono-atomic oxygen, zinc and aluminum atoms and atomic ions. The time-integrated spectra as well as the time-resolved spectra of the plasma emission indicate that the oxygen species in the ECR oxygen plasma experience additional excitation by the expanding ablation plumes, and the ablated species are excited frequently when traveling accompanying the plume expansion in the oxygen plasma, making the formed plasma highly excited and very reactive, which plays an important role in the reactive growth of ZnO matrix and the in-situ doping of Al into the growing ZnO matrix. The deposited ZnO and AZO films were evaluated for composition analysis by energy dispersive X-ray spectroscopy, structure characterization by X-ray diffraction and optical transmission measurement. The deposited ZnO is slightly rich in O. The Al concentration of the AZO films can be controlled and varied simply by changing the repetition rate of the laser used for Al target ablation. Both the ZnO and the AZO films are featured with hexagonal wurtzite crystal structure and exhibit high optical transparency in a wide spectral region. Al doping results in an improvement in the ultraviolet transparency, a blue shift in the absorption edge and a widening of the band gap.



## 1. Introduction

With a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, together with the excellent combined properties such as high transparency, conductivity, and thermal and chemical stability [1,2], ZnO has potential applications in short-wavelength optics and optoelectronics and is a promising material used for the fabrication of short-wavelength devices such as blue-ultraviolet (UV) light-emitting diodes, UV lasers and detectors [3–5], as well as used as transparent windows and electrodes in optoelectronic devices [6,7]. Moreover, ZnO can be doped with different elements and the properties of ZnO can also be significantly changed by doping. The conductivity of ZnO can be increased by extrinsic doping with Group III elements such as B, Ga, Al or In [8–10]. The band gap can be widened by doping with Al and Mg, and hence the optical transparency of ZnO in the UV region can be improved and the spectral region of UV photo-response can be extended [11,12]. Al doping of ZnO, in particular, has been studied extensively. Al-doped ZnO (AZO) shows similar properties of indium tin oxide (ITO) such as high electrical conductivity and optical transparency in the visible region [11,13–15] and is the most promising alternative materials to the widely used ITO and fluorine-doped tin oxide (FTO) because of its low cost, non-toxicity and high chemical stability.

ZnO and AZO thin films can be prepared by a variety of techniques including metal-organic chemical vapor deposition, sputter deposition, atomic layer deposition and pulsed laser deposition (PLD). Among these methods, PLD has been established as an effective technique for the fabrication of various materials with different compositions and

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http://dx.doi.org/10.1016/j.sab.2016.09.003
0584-8547/

structures [16]. In the PLD method, a pulsed laser beam is used as an energy source to ablate a target or vaporize the target surface. Pulsed laser ablation (PLA) of a target induces a fast expanding plume which composes of a mixture of energetic species ablated from the target. Accompanying the expansion of the plume, the ablated species transport to a nearby substrate, accumulate, nucleate and grow as a film on the substrate surface. PLD uses the plume induced by PLA as a material source for thin film deposition [16,17]. When target ablation is performed in a reactive gaseous environment, the species ablated from the target undergo a reactive expansion [18–22], and hence compound films can be synthesized through reactive deposition [23]. Low-temperature reactive plasmas are particularly attractive for providing reactive gaseous environments for plasma-based or plasma-assisted reactive fabrication of various materials including films and nanostructures [24–27]. Electron cyclotron resonance (ECR) microwave discharge is one of the most efficient techniques of gas discharge for generating plasma (usually called ECR plasma) [28]. With high degree of ionization and high concentration of reactive species, ECR plasmas have been combined with other techniques, accomplishing the so-called plasma-assisted synthesis techniques such as ECR plasma-enhanced chemical vapor deposition [29–31], and ECR plasma-assisted molecular beam epitaxy [32–34]. ECR plasma-assisted PLD has been proved to be very effective for the deposition of compound films including ZnO films [35]. In an oxygen plasma generated by ECR microwave discharge of $O_2$ gas, a metallic Zn target was ablated by a pulsed laser beam. The ECR oxygen plasma provided a reactive oxygen environment for oxide formation. The Zn species ablated from the Zn target reacted with the active oxygen species in the oxygen plasma, forming precursors for ZnO film to grow on the substrate surface. Not only as a reactive oxygen environment, the ECR oxygen plasma also served as a low-energy reactive oxygen plasma stream which bombarded the growing film at the same time, enhancing surface reactions and film growth, like somewhat a low-energy ion assisted deposition [23,36,37]. Recently, we have demonstrated an in-situ doping method for the preparation of AZO thin films based on pulsed laser co-ablation of a Zn target and an Al target with the assistance of an ECR discharge-generated oxygen plasma [15]. In the environment of the oxygen plasma, the Zn and Al targets were ablated by two pulsed laser beams. The ablation of the Zn target in the oxygen plasma results in the reactive deposition of ZnO matrix, while the ablation of Al target provides Al dopants to be incorporated into the growing ZnO matrix at the same time.

During the deposition of ZnO films, an oxygen-zinc plasma is formed due to the interaction between the oxygen plasma and the zinc plume when the zinc plume induced by Zn ablation expands in the oxygen plasma. Similarly, an oxygen-zinc-aluminum plasma is formed during the deposition of AZO films upon the pulsed laser co-ablation of the Zn and Al targets and ECR discharge of $O_2$ gas due to the interaction between the oxygen plasma and the zinc and aluminum plumes. The plasmas formed during film deposition are very complicated, exhibiting unique temporal and spatial features, and contain various excited species originally present in the working $O_2$ gas and energetic species ablated from the targets. The properties of the deposited films are closely related to the dynamics and the composition of the formed plasmas. To elucidate the mechanisms responsible for film deposition using this method and improve the quality of the deposited films, a clear understanding of the plasmas formed during film deposition is required. Optical emission spectroscopy (OES) is a simple and effective technique for in-situ plasma characterization [18–22,38]. We have recently reported the spectroscopic characterization of the plasma formed during the deposition of $Al_xGa_{1-x}N$ films by pulsed laser co-ablation of Al and GaAs targets in combination with ECR discharge of $N_2$ gas [39]. In the present work, time-integrated and time-resolved OES measurements with space resolution were used to characterize the plasmas formed by the ablation of Zn target and co-ablation of Zn and Al targets in the ECR oxygen plasma, respectively, for a study on the process of the deposition of ZnO and AZO films.

## 2. Experimental details

The method used for the deposition of ZnO and AZO films has been described previously [15,35]. The experimental arrangement for film deposition and OES measurement is schematically shown in Fig. 1. After the discharge and deposition chambers were evacuated to the base pressure (~$1 \times 10^{-4}$ Pa), pure (99.999%) $O_2$ gas was fed into the discharge chamber at a flow rate of 35 sccm, providing a working pressure of $3.0 \times 10^{-2}$ Pa. A microwave (2.45 GHz) was guided into the discharge chamber to excite the $O_2$ working gas at electron cyclotron resonance to produce ECR oxygen plasma. The oxygen plasma was then introduced into the deposition chamber where a metallic Zn target (purity 99.999%) and a metallic Al target (purity 99.995%) were ablated separately by two focused laser beams (wavelength: 532 nm; pulse width: 5 ns) from two frequency-doubled Q-switched Nd:YAG lasers. The laser beams were incident on the target surfaces at an angle of 45° with a spot size of 1 $mm^2$ in area. The laser fluences on the Zn and Al targets were about 4 and 3 $J/cm^{-2}$, respectively. The laser delivering laser beam 1 for Zn ablation worked at a repetition of 10 Hz while the other laser delivering laser beam 2 for Al target ablation worked at 1 or 2 Hz. As shown in Fig. 1, the zinc and aluminum plumes generated by target ablation expanded in the oxygen plasma towards the pre-cleaned Si (100) or quartz substrate placed ~50 mm away from the target centers, forming an AZO film. Films deposited with the laser for Al ablation (laser beam 2) worked at 1 and 2 Hz are henceforth referred to as AZO1 and AZO2, respectively. When the laser beam ablating the Al target was blocked, a ZnO film without Al doping was deposited on the substrate.

The plasmas formed during film deposition were imaged onto the entrance slit of a 0.5-m focal length spectrometer (Acton Research, Spectra Pro 500i) with a quartz lens (f = 10 cm) and a UV–vis optical fiber bundle (Acton Research, ILG-455-020-1). Optical emission of the plasmas was resolved spectrally by the spectrometer, recorded by a gated intensified charge coupled device (ICCD) camera (Princeton Instruments, PI-Max 1KRB-FG-43) for time-integrated measurement, or by a photomultiplier (PMT, Hamamatsu, R955) in combination with a digital storage oscilloscope (Tektronix, TDS3022B) for time-resolved measurement. The output of the PMT was fed directly into the oscilloscope with an impedance of 50 Ω. For OES measurements, both lasers worked at 10 Hz and were synchronized by a digital delay/pulse generator (Stanford Research System, DG535) which was also used to trigger the ICCD camera and the oscilloscope with a proper delay time. To eliminate the scattered laser light and to get rid of occasional fluctuations, time-integrated spectra were taken after the end of the laser pulse and accumulated for 100 times. Unless otherwise specified, all the time-integrated spectra were obtained by integrating for 10 μs, while the temporal profiles recorded for time-resolved OES measurement were averaged over 128 times. By moving the light-collecting lens and the optical fiber bundle, space-resolved OES measurements were achieved at different distances of d1 and d2 normally away from the Zn and Al target surfaces, respectively, as shown schematically in the inset in Fig. 1.

The composition of the deposited films was analyzed by energy dispersive spectroscopy (EDS) using a Philips XL30FEG/EDAX system. The sample structure was characterized by X-ray diffraction (XRD) with a Rigaku D/MAX 2550 VB/PC X-ray diffractometer using Cu Kα radiation. The optical transmission spectra of the films deposited on transparent quartz substrates were measured with a Hitachi UV-3000 ultraviolet-near infrared spectrophotometer. Other properties of the deposited films have been reported in Ref. [15].

## 3. Results and discussion

### 3.1. Plasma characterization

The $O_2$ gas is highly excited by ECR microwave discharge, leading to the generation of an ECR oxygen plasma which is constant in time and